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<p>(21) International Application Number: PCT/US92/02139</p> <p>(22) International Filing Date: 25 March 1992 (25.03.92)</p> <p>(30) Priority data: 677,068 29 March 1991 (29.03.91) US</p> <p>(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventor: PANKRATZ, Richard, Paul ; 167 Brookhill Lane, Circleville, OH 43113 (US).</p> <p>(74) Agent: GOLIAN, Andrew, G.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: POLYESTER FILM COATED WITH METAL ADHESION PROMOTING COPOLYESTER</p> <p>(57) Abstract</p> <p>An oriented polyester film coated on one or both sides with a copolyester derived from the condensation of isophthalic acid, terephthalic acid, an aliphatic dicarboxylic acid and a copolymerizable alkylene glycol and having a glass transition temperature (T_g) of at least 30 °C. The coated film provides excellent adhesion to vapor deposited metal coatings.</p>		

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TITLEPOLYESTER FILM COATED WITH METAL
ADHESION PROMOTING COPOLYESTER

5

BACKGROUND OF THE INVENTION

The present invention relates to an oriented polyester film coated on one or both sides with a copolyester primer coating for improving the adhesion of the polyester film to metals applied by vapor deposition.

Metallic coated polyester films have utility in various packaging and solar control applications. The commercial acceptance of such metal coated films, however, depends on obtaining good adhesion between the metallic layer and the polyester film.

One approach for improving the adhesion of the vapor deposited metal layer to the polyester film is disclosed in U.S. 4,476,189 issued to Posey et al. on October 9, 1984. U.S. 4,476,189 discloses a polyester film coated with a water-dispersible copolyester primer composition comprising terephthalic acid, an aliphatic dicarboxylic acid, and an aromatic sulfonated monomer with an alkylene glycol. Such primer compositions containing an aromatic sulfonated monomer provide inferior wet adhesion properties when used to bond polyester film to a vapor deposited metal. Moreover, such primer coated polyester film compositions are not recyclable for use in food contact applications because the sulfonated monomer is not FDA approved.

Accordingly, it is an object of this invention to provide an oriented polyester film having enhanced

adhesion to a vapor deposited metal for use in packaging applications.

Another object of this invention is to provide a copolyester coating composition for biaxially oriented polyethylene terephthalate film which renders the film more adhesive to vapor deposited metals.

SUMMARY OF THE INVENTION

The present invention relates to an oriented polyester film coated on one or both sides with a continuous copolyester coating consisting essentially of the condensation product of a diacid component selected from the group consisting of isophthalic acid, terephthalic acid and an aliphatic dicarboxylic acid of the formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ wherein n is 2 to 11, the total amount of the diacid component being 50 mole %; and a copolymerizable aliphatic or cycloaliphatic alkylene glycol component having from 2 to 11 carbon atoms, the total amount of the glycol component being 50 mole %; wherein said copolyester has a glass transition temperature (T_g) of at least 30°C but not higher than a temperature which is 100°C lower than the melting point of the copolyester, said film having improved adhesion to a further metal coating applied by vapor deposition.

DETAILED DESCRIPTION OF THE INVENTION

The polyester films for use in the invention include polyethylene terephthalate (PET), polyethylene-2,6-naphthalate and poly-1,4-cyclohexylenedimethylene terephthalate. Of these PET is most preferred. Copolyesters predominantly containing ethylene terephthalate units can also be used, which copolyesters

may contain a minor proportion, preferable not larger than 5 mole %, of dicarboxylic acid components other than terephthalic acid, such as isophthalic acid, sebacic acid and adipic acid, and which may also contain
5 a minor proportion, preferably not larger than 5 mole %, of diol components other than ethylene glycol, such as butanediol, diethylene glycol, triethylene glycol and 1,4-cyclohexanedimethanol. Such polyester films are made by procedures that are well-known in the art.

10 For example, the polyester resin may be melted and extruded as an amorphous sheet onto a polished revolving casting drum to form a cast sheet of polymer. Then, the cast sheet may be axially stretched in one direction, either in the direction of extrusion (longitudinal
15 direction) or perpendicular to the direction of extrusion (transverse direction) in the case of monoaxially oriented film and in two directions in the case of biaxially oriented film, i.e., the film is stretched in both the longitudinal and transverse
20 directions either consecutively or simultaneously. The first stretching step of the cast sheet may be in either of these two orthogonal directions. The amount of stretching, necessary to impart strength and toughness to the film, can range from 3.0 to 5.0 times the
25 original cast sheet dimensions in one or both directions. Preferably, the amount of stretching ranges from about 3.2 to 4.2 times the original cast sheet dimensions. The stretching operations are carried out at temperatures ranging from about the second order
30 transition temperature to below the temperature at which the polymer softens and melts.

If necessary, the film can be heat treated, after stretching, for a period of time sufficient to crystallize the polyester film. Crystallization imparts

stability and good tensile properties to the film. When polyethylene terephthalate is heat treated, it is subjected to a temperature ranging from 190°C to 240°C and, more preferably, a temperature ranging from 215°C to 235°C.

The coating copolyesters of the invention are produced by polycondensing a diacid component selected from the group consisting of terephthalic acid, isophthalic acid and an aliphatic dicarboxylic acid having the formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ wherein n is 2 to 11 with a glycol component selected from the group consisting of aliphatic and cycloaliphatic alkylene glycols having from 2 to 11 carbon atoms. The total amount of diacid used should be substantially equivalent to the total amount of glycol used on a molar basis, i.e., 50 mole % diacid to 50 mole % glycol.

Preferred copolyesters contain from 0 to 45 mole % isophthalic acid, from 40 to 85 mole % terephthalic acid, from 0 to 30 mole % of an aliphatic dicarboxylic acid, from 30 to 100 mole % of ethylene glycol and from 0 to 70 mole % of an aliphatic or cycloaliphatic alkylene glycol.

Representative aliphatic dicarboxylic acids used in the invention copolyesters include adipic, succinic, malonic, maleic, fumaric, azelaic, glutaric, sebacic, suberic, itaconic and dodecanedioic acids. Azelaic acid is preferred.

Examples of aliphatic or cycloaliphatic alkylene glycols used in the invention copolyesters include ethylene glycol, 1,3-propanediol, 1,4-butanediol, diethylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol and 1,10-decanediol. Ethylene glycol is preferred.

It has unexpectedly been found that when relative molar proportions of terephthalic acid, isophthalic acid, aliphatic dicarboxylic acid and alkylene glycol components are selected within limits that provide a
5 copolyester glass transition temperature (T_g) of at least 30°C, a copolyester primed polyester film having excellent adhesion to a vapor deposited metal can be obtained. As the T_g increases above 30°C the adhesion to vapor deposited metal is dramatically improved;
10 whereas with copolyester T_g's below 30°C the adhesion to vapor deposited metal is markedly decreased. Copolyesters having the specified diacid and glycol components and glass transition temperatures ranging from 30°C up to 100°C below the melting point of the
15 copolyester when used in making the coated primer film of the invention provide excellent adhesion to vapor deposited metal.

Preferred coating copolyesters of the invention include a copolyester derived from 85 mole %
20 terephthalic acid, 15 mole % isophthalic acid, 58 mole % ethylene glycol and 42 mole % neopentyl glycol having a T_g of 74°C; a copolyester derived from 80 mole % terephthalic acid, 20 mole % isophthalic acid and 100 mole % ethylene glycol having a T_g of 70°C; a
25 copolyester derived from 80 mole % terephthalic acid, 20 mole % azelaic acid, 35 mole % ethylene glycol and 65 mole % neopentyl glycol having a T_g of 66°C; a copolyester derived from 41 mole % terephthalic acid, 41 mole % isophthalic acid, 18 mole % azelaic acid and 100
30 mole % ethylene glycol having a T_g of 39°C; and a copolyester derived from 40 mole % terephthalic acid, 40 mole % isophthalic acid, 10 mole % adipic acid, 10 mole % azelaic acid and 100 mole % ethylene glycol having a T_g of 30°C. In the above numerical values the acid mole

percent is on the basis of total diacid while the glycol mole percent is on the basis of total glycol.

The copolyester coating of this invention may be applied in-line as a solvent solution or an aqueous dispersion at any stage during polyester film manufacture. The preparation of such coating solutions or dispersions is well-known in the art, for example, as disclosed in U.S. 4,888,381 and U.S. 3,054,703. The coating may be applied prior to stretching at a point after casting of the amorphous sheet and before uniaxial or biaxial stretching, or subsequent to the uniaxial stretching but prior to biaxial stretching. The heat applied to the coated film during the stretching stages is usually sufficient to evaporate the volatiles and dry the coating. The coating may also be applied off-line subsequent to biaxial stretching of the film, which necessitates a separate drying step.

The solvent or aqueous coating composition may be applied to the polyester film by any of the well-known techniques used in polyester film manufacture, e.g., by roller coating, spray coating, slot coating, immersion coating or, preferably, gravure roller coating. Moreover, the polyester film surface can be subjected to a corona discharge treatment prior to coating which permits the coating to more easily wet the surface, thereby improving the adhesion of the coating to the polyester film surface.

The solvent or aqueous coating composition may be applied to one or both sides of the polyester film, or it may be applied to one side and a different coating applied to the opposite side.

In some cases, from 5 to 10% of an isocyanate crosslinking agent may be added to the coating composition to harden the coating, thereby increasing

the Tg and further improving adhesion to the vapor deposited metal. The coating composition may also include antioxidants, dyes, pigments, lubricants, anti-blocking agents and/or slip agents, e.g., talc, metal
5 oxides, calcium carbonate, silica, titanium dioxide, silicates, aluminates and aluminosilicates.

The coating composition may be applied to the polyester film to produce a final dry coating thickness ranging from 1×10^{-6} to 5×10^{-4} inch, which corresponds
10 to a dry coating weight ranging from 0.03 to 15 g/m².

Polyester film which has been coated with the copolyester coating composition of this invention has excellent utility as a base for the production of metallized polyester films. Such films are prepared by
15 forming a metallic coating on a surface of the copolyester coated film by directing a stream of metal vapor or atoms onto the surface of the film by a vacuum deposition procedure. This is effected by heating the metal in a high vacuum, preferably in the range from
20 about 10^{-3} to 10^{-5} torr, to a temperature around its melting point such that the vapor pressure of the metal exceeds about 10^{-2} torr or by subjecting the metal to a stream of bombarding ions whereby the metal is removed by mass transfer "sputtering". The metal is
25 subsequently vaporized or sputtered, emitting metal vapors or atoms in all directions which impinge on the film surface, condense and form a thin metallic coating on the film. Applicable metals include zinc, nickel, silver, copper, gold, indium, tin, stainless steel,
30 chromium, titanium and, most preferably, aluminum, as well as the oxides of these metals. The thickness of the applied metal coating depends on the final use of the metallized film. Thicknesses of aluminum for use in

packaging applications range from about 100 to 2000 angstroms.

The advantageous properties of this invention can be observed by reference to the following examples which
5 illustrate, but do not limit, the invention. All parts and percentages are by weight unless otherwise indicated.

Examples 1 to 5 (Comparative Examples 1C to 5C)

10

A series of copolyesters having the compositions shown in Table 1 were applied as 0.5% solutions in methylene chloride to one surface of a 3 mil biaxially oriented polyethylene terephthalate film. The
15 crosslinked samples also contained 5% or 10% by weight of an isocyanate crosslinking agent (based on polyester solids). The copolyester coated films were dried at 50°C for one minute and aged for 24 hours at ambient temperature before metallizing. The coating weights
20 were 0.1 gm/m².

Metal adhesion was evaluated by placing samples of the coated films in a laboratory vacuum coater. The vacuum chamber was evacuated to less than 2×10^{-5} torr pressure and approximately 800 angstroms of aluminum was
25 evaporated onto the coated film surface from a tungsten filament.

The samples were further evaluated by heat sealing a polyester film having a heat-sealable copolyester on one surface (Melinex® 850 purchased from Imperial
30 Chemicals Corporation) to the metallized PET at 120°C and 20 psi for 5 seconds. Peel strengths (180°C) were used to quantitatively measure adhesion after the laminated samples had been aged for 24 hours. Adhesion

results are given in Table 1 together with the % of aluminum removed from the samples.

As can be readily seen from Table 1, PET film coated with the invention copolyesters of Examples 1 to 5 specifically formulated to have Tg's above 30°C exhibit significant improvement in metal adhesion as compared with uncoated PET film (the control) and with the copolyesters of Comparative Examples 1C to 5C which have Tg's under 30°C and are outside of the invention.

TABLE IA

VAPOR DEPOSITED ALUMINUM ADHESION TO COPOLYESTER PRIMED FILM

	Example No.	Tg °C	Copolyester Composition ¹ (Mole %)						
			Glycol				Diacid		
			5%	10%	15%	20%	25%	30%	35%
10	Control (unprimed PET)	80	100	-	-	100	-	-	-
15	1	74	58	-	42	85	15	-	-
	2	70	100	-	-	80	20	-	-
	3	66	35	-	65	80	-	-	20
	4	39	100	-	-	41	41	-	18
	5	30	100	-	-	40	40	10	10
20	1C	19	57	-	43	33	33	-	34
	2C	10	96	4	-	50	20	-	30
	3C	-10	100	-	-	33	17	-	50
	4C	-15	100	-	-	55	-	-	45
	5C	-20	75	25	-	55	45	-	-

TABLE IB

VAPOR DEPOSITED ALUMINUM ADHESION TO COPOLYESTER PRIMED FILM

Aluminum Adhesion

5	Example No.	gm/in (% Al removed)		
		Uncross-linked	Cross-linker ²	Cross-linker ²
10	Control (unprimed PET)	110 (100)	---	---
	1	325 (0)	445 (0)	360 (0)
15	2	270 (0)	315 (0)	310 (0)
	3	335 (0)	360 (0)	280 (0)
	4	295 (80)	310 (80)	300 (0)
	5	235 (80)	235 (80)	260 (50)
	1C	27 (90)	42 (90)	40 (80)
20	2C	50 (90)	75 (60)	97 (80)
	3C	52 (90)	77 (90)	115 (90)
	4C	20 (90)	100 (50)	70 (90)
	5C	27 (90)	17 (80)	17 (70)
25	¹ ED - Ethylene Glycol T - Terephthalic Acid 4T - 1,4-Butanediol I - Isophthalic Acid NPG - Neopentyl Glycol AD - Adipic Acid AZ - Azealic Acid			
30	² Isocyanate crosslinking agent (weight %).			

Example 6 (Comparative Example 6C)

The copolyester of Example 3 was coated on PET film, the coated film was metallized as previously described and then both wet and dry adhesion were compared (Example 6C) to a commercially available copolyester (Hostaphan® 2600 purchased from American Hoechst Company) containing from 5 to 10% of a sulfonated isophthalic acid in the polymer.

The metal adhesion was evaluated by heat sealing an electrically discharge treated ethyl methacrylate film (Type 899 purchased from the Dow Chemical Company) to the metallized PET films at 120°C and 50 psi for 15 seconds. In the wet adhesion test, the laminates were first submerged in water for 1 minute, removed and then the peel strengths were measured.

Dry and wet adhesion results are given in Table 2 together with the % of aluminum removed from the samples.

Table 2

VAPOR DEPOSITED ALUMINUM ADHESION

Example Aluminum Adhesion (gm/in)

No. (% Al removed)

Dry Wet

6 925 (0) 626 (10)

6C 990 (0) 112 (95)

The results show that the copolyester of the invention has much better wet adhesion compared to the commercial copolyester.

What is claimed is:

1. An oriented polyester film coated on one or both sides with a continuous copolyester coating consisting essentially of the condensation product of a diacid component selected from the group consisting of isophthalic acid, terephthalic acid and an aliphatic dicarboxylic acid of the formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ wherein n is 2 to 11, the total amount of the diacid component being 50 mole %; and a copolymerizable aliphatic or cycloaliphatic alkylene glycol component having from 2 to 11 carbon atoms, the total amount of the glycol component being 50 mole %; wherein said copolyester has a glass transition temperature (T_g) of at least 30°C but not higher than a temperature which is 100°C lower than the melting point of the copolyester, said film having improved adhesion to a metal coating applied by vapor deposition.

2. The film of claim 1 wherein the copolyester consists essentially of the condensation product of on the basis of diacid 85 mole % terephthalic acid, 15 mole % isophthalic acid, and on the basis of glycol, 58 mole % ethylene glycol and 42 mole % neopentyl glycol.

3. The film of claim 1 wherein the copolyester consists essentially of the condensation product of on the basis of diacid 80 mole % terephthalic acid, 20 mole % isophthalic acid and on the basis of glycol 100 mole % ethylene glycol.

4. The film of claim 1 wherein the copolyester consists essentially of the condensation product of on the basis of diacid 80 mole % terephthalic acid, 20 mole % azelaic acid, and on the basis of glycol 35 mole % ethylene glycol and 65 mole % neopentyl glycol.

5. The film of claim 1 wherein the copolyester consists essentially of the condensation product of on

the basis of diacid 41 mole % terephthalic acid, 41 mole % isophthalic acid, 18 mole % azelaic acid and on the basis of glycol 100 mole % ethylene glycol.

5 6. The film of claim 1 wherein the copolyester consists essentially of the condensation product of on the basis of diacid 40 mole % terephthalic acid, 40 mole % isophthalic acid, 10 mole % adipic acid, 10 mole % azelaic acid and on the basis of glycol 100 mole % ethylene glycol.

10 7. A metallized polyester film comprising an oriented polyester base film coated on one or both sides with (a) a continuous copolyester coating consisting essentially of the condensation product of a diacid component selected from the group consisting of
15 isophthalic acid, terephthalic acid and an aliphatic dicarboxylic acid of the formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ wherein n is 2 to 11, the total amount of the diacid component being 50 mole %; and a copolymerizable aliphatic or cycloaliphatic alkylene glycol component having from 2
20 to 11 carbon atoms, the total amount of the glycol component being 50 mole %; wherein said copolyester has a glass transition temperature (T_g) of at least 30°C but not higher than a temperature which is 100°C lower than the melting point of the copolyester and (b) a vapor
25 deposited metal coating on the copolyester coating.

8. The film of claims 1 or 7 wherein the polyester base film is polyethylene terephthalate.

9. The metallized film of claim 7 wherein the polyester base film is polyethylene-2,6-naphthalate.

30 10. The metallized film of claim 7 wherein the metal is zinc, nickel, silver, copper, gold, indium, tin, stainless steel, chromium, titanium and aluminum.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/02139

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 J 5/18, 7/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 08 J	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4888381 (R.P. PANKRATZ) 19 December 1989, see column 1, line 60 - column 2, line 53	1-6
Y	---	1-9
Y	US, A, 4493872 (F.G. FUNDERBURK ET AL.) 15 January 1985, see column 6, line 15 - line 16; claims 1-5,16	1-9
Y	EP, A2, 0379190 (TOYO BOSEKI KABUSHIKI KAISHA) 25 July 1990, see page 4, line 44 - page 5, line 1	1-9
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25th June 1992	05. 08. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	I-K PETERSSON	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4971863 (C.R. HART) 20 November 1990, see claim 1 --	1-10
A	EP, A2, 0316620 (HOECHST CELANESE) 24 May 1989, see page 3, line 55 - line 56; page 4, line 27 - line 28; page 5, line 20 - line 21 --	1-10
A	Dialog Information Service, File 351, WPI, Dialog accession no. 008140314, WPI accession no. 90-027315/04 (TORA), "Composite films for plastic cards - comprising copolymerised polyester(s) contg. inorganic granules having specified crystal-fusion heat.", & JP,A,1306430, publ.891211 -- -----	1-10

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 92/02139

SA 58727

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4888381	19/12/89	NONE	
US-A- 4493872	15/01/85	CA-A- 1230721	29/12/87
		EP-A-B- 0144878	19/06/85
		EP-A- 0322529	05/07/89
		JP-B- 1054192	17/11/89
		JP-A- 60198240	07/10/85
EP-A2- 0379190	25/07/90	JP-A- 2190333	26/07/90
		JP-A- 3081151	05/04/91
		JP-A- 3118152	20/05/91
		JP-A- 3169549	23/07/91
		JP-A- 3175035	30/07/91
		JP-A- 3176146	31/07/91
US-A- 4971863	20/11/90	EP-A- 0348062	27/12/89
		JP-A- 2050828	20/02/90
EP-A2- 0316620	24/05/89	JP-A- 1198642	10/08/89
		SE-A- 8803951	31/10/88
		US-A- 4880695	14/11/89
		US-A- 4923713	08/05/90

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